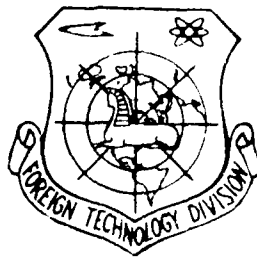


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EFFECT OF URANIUM AND IRON IONS ON CORROSION OF TITANIUM IN SULFURIC ACID SOLUTIONS

by



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EDITED TRANSLATION

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TITANIUM IN SULFURIC ACID SOLUTIONS

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<p>ABSTRACT (U) Ions of uranium (valence plus 6) and iron (valence plus 3) were introduced as uranium oxide sulfate and iron sulfate in sulfuric acid solution by boiling the acid in contact with both metals. Anodic polarization curves of Ti were obtained by potentiostatic methods, and cathodic curves by galvanostatic methods. Potentials were obtained by the H electrode. The introduction of these metal ions in the sulfuric acid solution leads to a marked decrease of corrosion on Ti, equiv. to a passivation. A sudden displacement of the Ti potential into the pos. region is achieved simultaneously with the depression of its corrosion by the introduction of sufficient uranium (valence plus 6) and iron (valence plus 3). The potential displacement is dependent upon the concn. of uranium (valence plus 6) and iron (valence plus 3). The iron (valence plus 3) has a greater effect, displacing the potential by 1-1.5 v., the uranium (valence plus 6) no more than 0.6-0.7 v. Differing corrosion rates and the formation of passivating films are the results of these potential displacements. The cathodic polarization curves for Ti in the presence of uranium (valence plus 6) and iron (valence plus 3) in sulfuric acid solutions, as a function of the diffusion limited current, pass through significant higher pos. potentials than in the absence of these ions. The threshold current increases with the increase of uranium (valence plus 6) and iron (valence plus 3) concn. Iron (valence plus 3) is the more passivating ion. These ions are cathodic depolarizers; they facilitate the cathodic process significantly and achieve an adequate potential displacement into the passive region.</p>				

EFFECT OF URANIUM AND IRON IONS ON CORROSION OF TITANIUM IN SULFURIC ACID SOLUTIONS

A. S. Gryaznova and M. M. Kurmenov

Titanium, because of the ease with which it can be passivated in a number of aggressive media, possesses high corrosion resistance [1-3]. However, in sulfuric acid titanium preserves its stability only in dilute (to 5%) solutions at low temperatures. In acid solutions of higher concentration and at elevated temperatures titanium dissolves from the active state at high rates of the reaction.

Recently in works [3-6] it was disclosed that with the introduction of Fe^{3+} ions into dilute solutions of sulfuric acid at low temperature a passive state and a lowering of the rate of titanium corrosion are attained.

No information about the influence of ions of uranium on the corrosion of titanium is to be found in literature. Most authors connect the passivating capacity of Fe^{3+} ions with facilitation of the course of the cathode process and with anode passivity which occurs in this situation.

Our problem included the study of the effect of U^{6+} and Fe^{3+} ions on the passivation of titanium in boiling solutions of sulfuric acid.

Experiment

We investigated the effect of U^{6+} and Fe^{3+} ions on the corrosion and electrochemical behavior of BT-1 (VT-1) titanium in a 1-3 M solution of H_2SO_4 at boiling temperature, which made it possible to follow the change in the potential of titanium with an increase in the concentration of metal cations in the transition from the active to the passive state. In this situation the cations of the metals uranium and iron were introduced into the acid solution in the form of the sulfate compounds UO_2SO_4 and $Fe_2(SO_4)_3$.

Anode polarization curves of titanium were obtained by the potentiostatic method and the cathode curves, by the galvanostatic method. The potentials are given in accordance with the hydrogen electrode.

Results and Their Evaluation

From the results given in Fig. 1 on the study of the influence of U^{6+} and Fe^{3+} ions on the rate of corrosion of titanium in solutions of H_2SO_4 it is seen that the introduction of these ions into boiling acid solutions leads to a lessening of the corrosion of the metal. There exists, however, a difference in the passivation of the corrosion of titanium by the U^{6+} and Fe^{3+} ions; a more significant lowering of the corrosion of titanium is obtained with the introduction of Fe^{3+} ions into the acid solutions. There is an optimal concentration of U^{6+} and Fe^{3+} ions with which stable passivation of titanium is assured. With the introduction of these ions in insufficient quantity (below 0.5 g/l for Fe^{3+} and 1 g/l for U^{6+}) no marked change in the rate of corrosion of the titanium is observed. Simultaneously with the lessening of the titanium corrosion rate with the introduction of U^{6+} and Fe^{3+} ions into solutions there occurs a sharp shifting of the potential of the metal into the positive area (Fig. 2). This shift of the potential depends on the nature of the metal cation introduced into the solution and is brought about by the potential of the process of reduction of the Fe^{3+} and U^{6+} . A greater displacement of the potential is attained with the introduction of Fe^{3+} into the solution. The potential of titanium

in this case changes by 1-1.5 V, while with the introduction of U^{6+} it becomes more positive by 0.6-0.7 V. Such a difference in the Ti potential shift due to Fe^{3+} and U^{6+} ions is characterized also by a different rate of Ti corrosion from the passive state, differing by an order; this is apparently connected with the formation on its surface of passivating films with different corrosion resistances.

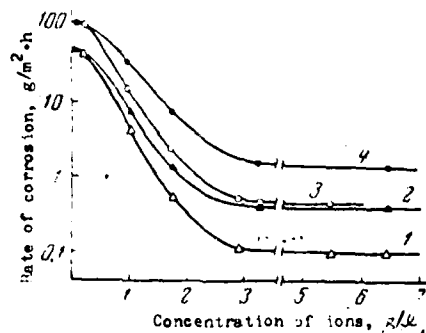


Fig. 1. Effect of Fe^{3+} and U^{6+} ions on the rate of corrosion of Ti in boiling solutions of H_2SO_4 :

1 - 1 M H_2SO_4 ; 2 - 1 M $H_2SO_4 + U^{6+}$; 3 - 2 M $H_2SO_4 + Fe^{3+}$; 4 - 2 M $H_2SO_4 + U^{6+}$.

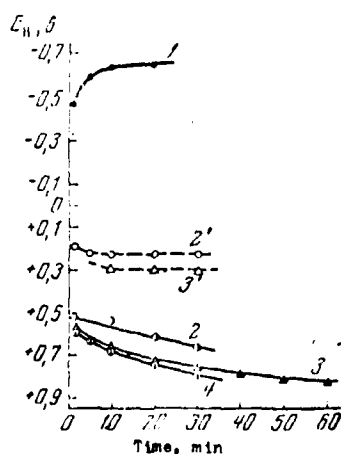


Fig. 2. Change in Ti potential with time in 1 M boiling solutions of H_2SO_4 , depending on U^{6+} and Fe^{3+} concentration: 1 - without additive; 2 - with addition of 3.25 g/l U^{6+} ; 3 - 6.5 g/l U^{6+} ; 4 - 0.28 g/l Fe^{3+} ; 5 - 5.6 g/l Fe^{3+} ; 6 - 11.2 g/l Fe^{3+} .

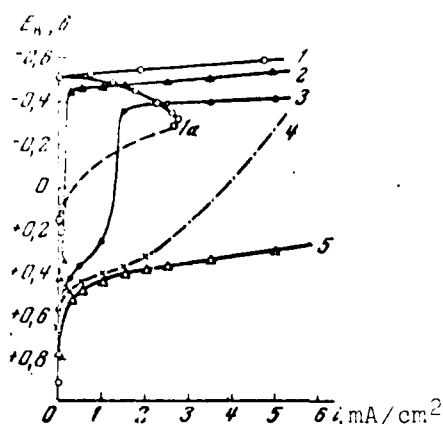


Fig. 3. Polarization curves of Ti, taken in boiling 1 M solutions of H_2SO_4 depending on Fe^{3+} ion concentration. 1 and 1a -- cathode and anode curves taken in acid without addition of Fe^{3+} ions. Cathode curves taken in acid with Fe^{3+} additions; 2 -- 0.28 g/l; 3 -- 2.8 g/l; 4 -- 5.6 g/l; 5 -- 11.2 g/l.

Anode polarization curves of titanium in a boiling 1 M H_2SO_4 solution (Figs. 3 and 4) have a form which is typical for metals and alloys which are inclined to anode passivity. In the region of negative potentials on a polarization curve the loop of anode solution is fixed. As the experiments showed, with an increase in the acid concentration of up to 3 M the maximum passivation current for titanium is more than doubled. In this situation the potential of the beginning of passivation is displaced by 80-100 mV to the positive side. Beyond the section of active solution of titanium there is a region of active-passive state, whereupon the anode passivity sets in, brought about by the formation on the surface of the titanium mainly of phase films. The rate of titanium corrosion is independent of potential over a broad range of potentials.

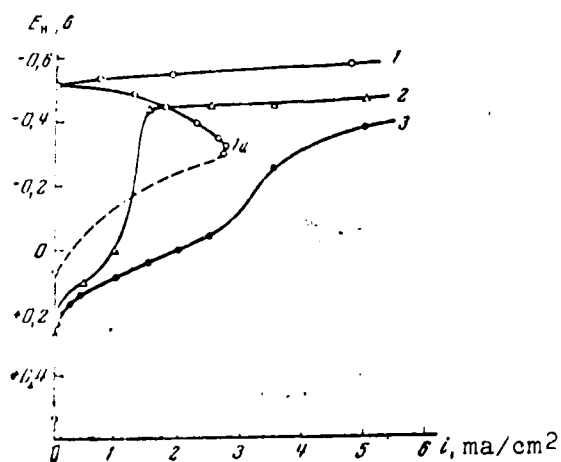


Fig. 4. Polarization curves of Ti taken in boiling 1 M solutions of H_2SO_4 , depending on U^{6+} ion concentration. 1 and 1a -- cathode and anode curves taken in acid without the addition of U^{6+} ions. Cathode curves taken in acid with U^{6+} ; 2 -- 3.25 g/l; 3 -- 6.5 g/l.

The curves of cathode polarization of titanium with the introduction of U^{6+} and Fe^{3+} ions into solutions of H_2SO_4 (see Figs. 3 and 4) up to the limiting diffusion current lie at considerably higher positive potentials than for acids without addition of these ions. In these parts of the cathode curves reduction of the uranium and iron ions occurs, with formation of ions of lower valence (U^{4+} , Fe^{2+}). The strength of the limiting diffusion current depends on the nature of the cation and its content in the solution. With an increase in the concentration of U^{6+} and Fe^{3+} ions in the solution the limiting current increases. However, the limiting current increases more slowly with the U^{6+} ion in the solution than in the presence of the Fe^{3+} ion. This indicates that the Fe^{3+} ion is a more effective passivator than the U^{6+} ion.

The experimental results obtained show that the ions U^{6+} and Fe^{3+} are effective cathode depolarizers, that they significantly facilitate the cathode process, and that because their oxidizing-reducing potential lies in the region of the passive state, they bring about a corresponding displacement of the potential of titanium into the passive area. Apparently, the influence of other ions of polyvalent metals, for example, ions of Cr^{6+} and Mn^{7+} , on the passivation of titanium in H_2SO_4 solutions will be analogous to the influence of the U^{6+} and Fe^{3+} ions. For conversion of titanium into the stable passive state it is necessary that the cathode current for reduction of ions of metals with varying valence exceed than the maximum current of the anode solution of titanium.

Conclusions

1. The introduction of U^{6+} and Fe^{3+} ions into boiling solutions of dilute H_2SO_4 brings about a sharp reduction in the rate of corrosion of titanium. The Fe^{3+} ion is a more effective passivator of titanium in boiling H_2SO_4 solutions than the U^{6+} ion.

2. The passivating capacity of U^{6+} and Fe^{3+} ions is connected with the displacement of the potential of titanium into the passive

region, due to facilitation of the cathode process and also to the high oxidation-reduction potential of a solution containing U^{6+} and Fe^{3+} ions.

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